the question of how far one can go in utilizing the results of exchange experiments to deduce the gross rate of reaction. Further experimental and theoretical work would be strongly indicated.

Acknowledgment.—The authors wish to express appreciation to Drs. E. L. King and H. Taube for stimulating discussions of this work.

LEMONT, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

Phase Equilibria of Uranium Trioxide and Aqueous Hydrofluoric Acid in Stoichiometric Concentrations[1]

BY WILLIAM L. MARSHALL, J. S. GILL AND C. H. SECOY

RECEIVED APRIL 12, 1954

A phase study of the liquid–solid equilibria for aqueous solutions containing two moles of hydrofluoric acid per mole of uranium trioxide from the ice eutectic at $-13°$ to the critical temperature of the saturated liquid at 377° is presented. Some observations on vapor–liquid equilibria are included and their significance is discussed. The system displays three solid phases of uranyl fluoride hydrates stable with respect to the saturated solution in the temperature ranges -13 to 150°, 150 to 240°, and above 240°, respectively. There is some evidence to indicate that these solids are all allotropic modifications of uranyl fluoride dihydrate but this is not certain. In the dilute region at temperatures above approximately 200° a solid phase appears which is apparently a solid solution between $UO_2(OH)_2$ and $UO_2(OH)F \cdot {}^1/_2H_2O$. A two-liquid phase region occurs from approximately 23 to 66 weight per cent. uranium trioxide. The critical solution temperature of the two-liquid phase region is 320° while the upper limit is the temperature of the invariant system solid–liquid I–liquid II–vapor, at 333°. The vapor–liquid critical temperature of the water-rich liquid phase saturated with respect to the high temperature solid is 376°, thus indicating a significant but small solubility in the critical fluid.

Introduction

Some solubility data for uranyl fluoride in water from 0 to 100° have been determined both by Kunin[2] and by Dean and Eidinoff.[2] Freezing point data for uranyl fluoride in water have been presented by Johnson and Kraus,[3] of this Laboratory. It was our objective to determine a phase equilibria picture for this system from the ice eutectic to the critical temperature of the aqueous phase. In carrying out this research we have found that some portions of the system at the higher temperatures cannot be considered as a simple two-component system but must be considered as a three-component system, probably best represented by UO_3, F_2O_{-1} and H_2O. This is true for two reasons: first, because the vapor phase undoubtedly contains HF as well as H_2O and second, because of the occurrence of a basic salt, $UO_2(OH)F \cdot {}^1/_2H_2O$, as a constituent of the solid. In this study the vapor phase has been neglected, compositions being those determined at 25°. In brief, the data presented herein indicate the phase changes which occur when stoichiometric uranyl fluoride solutions are heated in a closed system the volume of which is approximately 50% vapor at room temperature. Also, considerable insight into the general nature of the true phase diagram is obtained.

Experimental

Anhydrous uranyl fluoride was obtained both from the Harshaw Chemical Company and from the Y-12 Plant, Oak Ridge, Tennessee. A spectrographic analysis of both materials showed negligible impurities. The fluoride to uranium mole equivalent ratios were found by the Y-12 Plant Analytical Division to be 1.983 and 1.998, respectively.

Solubility data below 0° were obtained by standard methods of thermal analysis. A copper–constantan thermocouple was used for temperature measurements. Analytical solubility determinations were made from 0 to 90°. Solutions which were saturated with respect to solid were analyzed directly for uranium by ignition at 900° to U_3O_8; the precision of duplicates was within ±0.15%. Samples analyzed after four hours stirring time agree with those obtained after 24 hours or longer and thus indicated a fairly rapid equilibrium attainment.

The first work above 100° was carried out in sealed silica and Pyrex tubes using the technique described by Secoy.[4] Later, additional data were obtained in sealed tubes using a semi-micro technique described by Marshall, Wright and Secoy.[5] Both of these procedures entailed the synthetic method in which the temperature of a solution of known composition is changed and the point recorded at which a phase transition occurs. By this method solubility points were checked to ±1° for the rapidly reversible equilibria.

Owing to a very low temperature coefficient of solubility the synthetic method was not effective for concentrated solutions in the range 150 to 240°. Therefore, an analytical approach was attempted in which saturated solution and excess solid sealed in silica tubes were rocked in an aluminum heating block at a constant temperature, the variation in temperature being of the order of ±2°. The tubes were rapidly cooled in an ice-bath, opened, and both the gel-solid (originally liquid phase) and the crystalline-solid analyzed for uranium. Above 150° the saturated solution is very viscous but will flow in 5 millimeter, inside diameter, tubing. Below this temperature, if it is not shaken on cooling, the solution forms a translucent gel. The assumption was made that equilibria attainment during the cooling period is sufficiently slow under conditions of such high solution viscosity as to not materially change the solid and solution compositions.

The compositions of the solid phase in the dilute region JF of Fig. 1 were obtained by removing the solution from a steel pressure vessel at the equilibration temperature by means of steel capillary tubing, cooling the bomb to room temperature, removing the crystalline solid and analyzing it for uranium and fluoride.

Analysis for fluoride was carried out by dissolving the solid in a measured amount of standard acid, removing uranyl ion on a cation-exchange resin and titrating the resultant acid solution with standard base.[6]

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[1] Presented in part before the Division of Physical and Inorganic Chemistry at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April 8–12, 1951.

[2] J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," Part I, First Edition, National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 569.

[3] J. S. Johnson and K. A. Kraus, THIS JOURNAL, **74**, 4436 (1952).

[4] C. H. Secoy, *ibid.*, **72**, 3343 (1950).

[5] W. L. Marshall, H. W. Wright and C. H. Secoy, *J. Chem. Educ.*, **31**, 34 (1954).

[6] H. O. Day, Jr., E. V. Jones, J. S. Gill and W. L. Marshall, *Anal. Chem.*, **26**, 611 (1954).

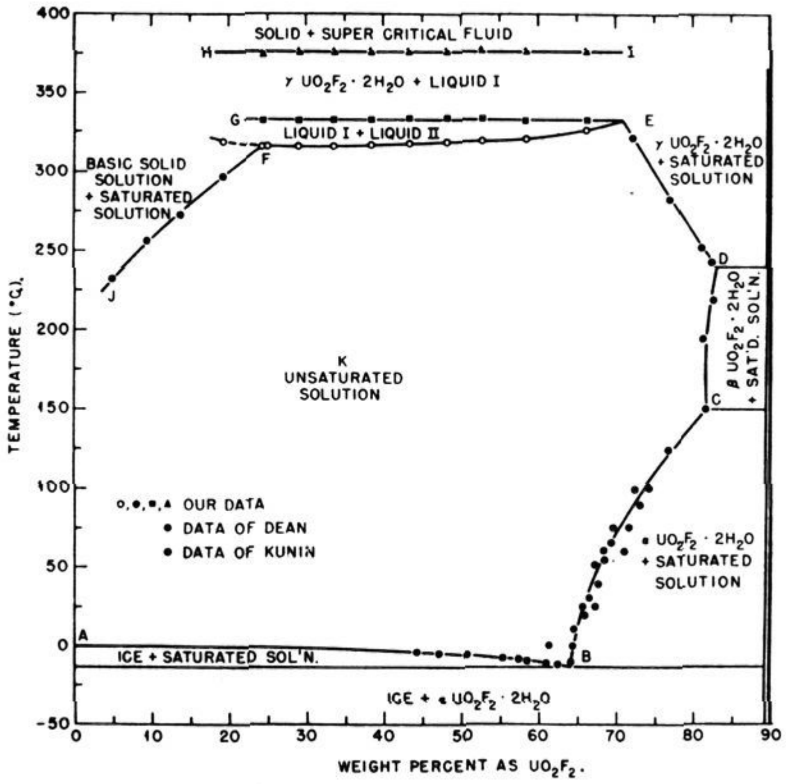

Fig. 1.—Phase equilibria of UO_3 and HF in stoichiometric concentrations (aqueous system).

The Data and Discussion

Temperatures at which phase transformations were observed are shown in Fig. 1. The experimental data are available on microfilm.[7]

Region K of Fig. 1 represents unsaturated solution for the system uranyl fluoride–water. The ice curve is shown by line AB to the eutectic point B. Line BCDE is the uranyl fluoride solubility curve, transitions occurring in the solid phase at C and at D. The solubility data of Kunin[2] and of Dean and Eidinoff[2] are compared to our data in the figure. Although a thorough study of these solid phases was not undertaken, analysis of each for uranium and fluoride indicated that all three have the composition $UO_2F_2{\cdot}2H_2O$. Therefore, they have been designated, respectively, α-, β- and γ-uranyl fluoride dihydrate. Because of the difficulty of obtaining samples and the relatively small weight factor of the water of hydration these compositions should be regarded as tentative. The solid phase below 150° appears as extremely fine, silky needles, whereas in the region 150–240° the crystals exhibit ability to grow to large sizes. An attempt was made to determine the structural system of these latter crystals. No success was attained using a polarizing microscope. It appeared that the individual crystal units at room temperature had rearranged within the macro-crystal to produce a pseudomorphic form which originally was either in the hexagonal or cubic system.

The invariant point temperature along GE was fixed by liquefaction upon lowering the temperature of the solid (γ $UO_2F_2{\cdot}2H_2O$) which is stable above line GE. Metastability above 333° of the uranium trioxide rich liquid phase prevented the point being fixed by raising the temperature.

The region immediately above line FE represents a two-liquid phase region. The minimum of the curve is not consolute in that the two phases involved at that point are not identical. The consolute temperature for the diagram occurs between 48.17 and 52.75% UO_2F_2. On the left of this point in Fig. 1 the UO_3 rich phase appears as a second liquid upon raising the temperature while on the right the new phase is the water rich liquid. Evidently, this point must be on the lower consolute solution curve of the ternary system, which curve crosses the temperature–concentration plane represented by Fig. 1 at a temperature near 320°.

The upper limit of the two-liquid phase region is at 333°, an invariant point at which vapor, liquid I, liquid II and solid coexist. In the region above 333° and below 376° there are two phases in the condensed system, water-rich liquid (L_I) and solid. Experimental temperatures representing the critical temperature (376°) of the saturated solution are

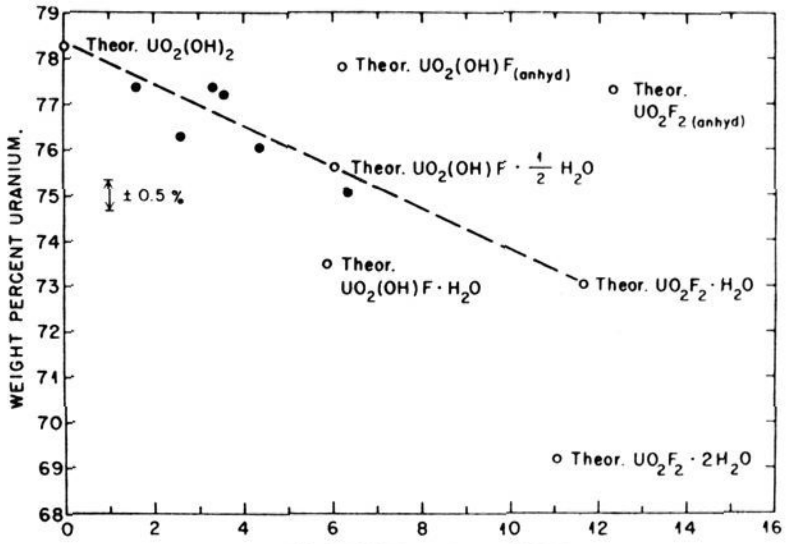

Fig. 2.—Composition of solid solution in system UO_3–HF–H_2O.

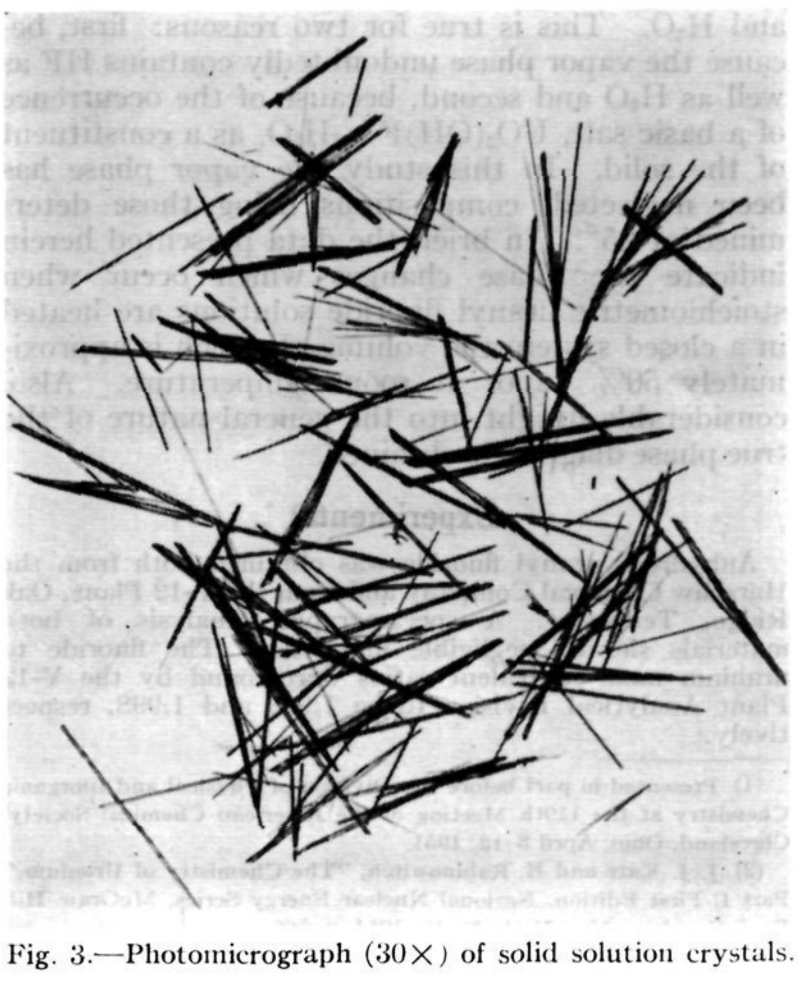

Fig. 3.—Photomicrograph (30×) of solid solution crystals.

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(7) The experimental data of this paper have been deposited as Document number 4289 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm, to Chief, Photoduplication Service, Library of Congress.

shown by points along HI and represent initial starting concentrations of solutions. Above line HI there is the supercritical fluid and solid. The critical point for pure water (374.2°) does not appear to have been elevated more than two or three degrees, thus indicating that the solubility of components in the water rich liquid is very low.

Solutions more dilute than approximately 25% UO_2F_2 yield a solid phase at temperatures indicated by line JF, well below the two-liquid phase region. Analyses of samples of this solid phase obtained from each of several different solution compositions show a continuous variation in the uranium to fluoride mole ratio as indicated by Fig. 2. The analytical data are available on microfilm.[7] From these results a solid solution of $UO_2(OH)_2$ and either $UO_2(OH)F \cdot {}^1/_2H_2O$ or $UO_2F_2 \cdot H_2O$ is indicated. Because of the similarity in size of the fluoride ion and the hydroxyl radical the possibility of the existence of such solid solutions was suggested by M. A. Bredig of this Laboratory. A comparison of X-ray diffraction data obtained by H. L. Yakel, also of this Laboratory, for this solid with data for α-$UO_2(OH)_2$ shows minor differences in structure entirely consistent with the solid solution hypothesis. A photomicrograph of this solid is shown in Fig. 3.

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Bis-cyclopentadienyl Compounds of Ti, Zr, V, Nb and Ta

BY G. WILKINSON AND J. M. BIRMINGHAM

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Bis-cyclopentadienyl halides of titanium, zirconium and vanadium in the IV oxidation state, and of niobium and tantalum n the V oxidation state, have been prepared by the reaction of the anhydrous metal halides with cyclopentadienylmagnesium halides or with cyclopentadienylsodium. The properties of the halides are given and the preparation of the ions $(C_5H_5)_2Ti^+$ and $(C_5H_5)_2V^+$ by reduction of the IV valent titanium and vanadium compounds in aqueous solution is described. The electronic structure of the derivatives is discussed briefly.

The existence of bis-cyclopentadienyl compounds of Cr(II), Fe(II, III), Ru(II, III), Co(II, III), Rh(III), Ir(III) and Ni(II, III) is well established[1] and preliminary notes on derivatives of Mn(II), Mo(IV, V) and W(IV, V) have been made recently.[2a,b] We now describe derivatives of titanium(III) and -(IV), of zirconium(IV), of vanadium(III) and -(IV), and of niobium and tantalum(V), some of which have been noted in a preliminary communication.[3]

I. Experimental

General Methods of Preparation.—Bis-cyclopentadienyl halides of Ti, Zr, V, Nb and Ta were made by the reaction of cyclopentadienylmagnesium chloride or bromide with the metal chloride or bromide, respectively, in benzene–ether solution. A more convenient alternative procedure, generally giving higher yields, was the reaction of cyclopentadienylsodium with the metal halide in either tetrahydrofuran or 1,2-dimethoxyethane (dimethyl "cellosolve") solution. In the Grignard method, cyclopentadienylmagnesium chloride or bromide was prepared from ether solutions of either *n*-propylmagnesium chloride or ethylmagnesium bromide, respectively. The theoretical amount of cyclopentadiene obtained by cracking dicyclopentadiene was added to the Grignard reagent (in some cases, most of the ether was first displaced by benzene), and the mixture was then warmed until gas evolution ceased (about 1 hr.); the solution was cooled in ice and was then slowly run into a solution or suspension of the metal halide in ether or benzene solution, with vigorous stirring and ice cooling. In the second method, cyclopentadienylsodium was prepared by adding the theoretical amount of cyclopentadiene to finely divided sodium in tetrahydrofuran or dimethyl "cellosolve." The mixture was stirred at room temperature until gas evolution ceased; the resulting orange solution was cooled and was run slowly into the solvent plus the metal halide, with rapid stirring and ice cooling. The halides VCl_4, $NbBr_5$ and $TaBr_5$ were prepared by the reaction of the free halogen upon the heated metals,[4] and were used without further purification; the other halides were commercially available.

The procedure employed for isolation of the bis-cyclopentadienyl compounds was very similar in all cases. After stirring the reaction mixture for 2–3 hours, the solvent was removed under reduced pressure. The residue was then repeatedly extracted with boiling chloroform through which was passed a slow stream of hydrogen chloride (for chloride preparations) or hydrogen bromide (for bromide preparations). The extract was evaporated and the residue re-extracted with chloroform saturated with hydrogen chloride or bromide. The second extract was worked up differently for the several compounds. For bis-cyclopentadienyltitanium(IV) chloride and bromide, the product was crystallized from toluene. For the bis-cyclopentadienyl halides of zirconium, vanadium, niobium and tantalum, the chloroform extract, after saturation with the appropriate hydrogen halide, was cooled in a Dry Ice–acetone-bath and the crystals separated by rapid filtration. Bis-cyclopentadienylzirconium(IV) bromide was recrystallized from carbon tetrachloride containing 25% chloroform. The bis-cyclopentadienyl halides of vanadium, niobium and tantalum were recrystallized from chloroform saturated with hydrogen chloride or bromide, by cooling the solutions to −70°. An alternative procedure for the isolation of the bis-cyclopentadienylniobium and tantalum bromides was to pour the reaction mixture into an ice slush of 6 *N* hydrobromic acid. The yellow aqueous phase, which contained bis-cyclopentadienylmetal hydroxy ions was treated with bromine water. The resulting yellow precipitate was centrifuged, washed with 1 *N* hydrobromic acid until free from magnesium or sodium salts, and dissolved in boiling 48% hydrobromic acid. This solution was distilled azeotropically with benzene in a stream of hydrogen bromide; after removal of excess benzene, the product was crystallized from chloroform as before.

The quantities of the reactants used and the yields of the compounds in typical preparations are shown in Table I.

Analyses.—For determination of the metals, the bis-cyclopentadienyl compounds were destroyed by fuming with

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[1] See G. Wilkinson, P. L. Pauson and F. A. Cotton, THIS JOURNAL, **76**, 1970 (1954), where references to previous works are given.

[2] (a) G. Wilkinson and F. A. Cotton, *Chemistry and Industry*, 307 (1954); (b) F. A. Cotton and G. Wilkinson, *Z. Naturforsch.*, in press.

[3] G. Wilkinson, P. L. Pauson, J. M. Birmingham and F. A. Cotton, THIS JOURNAL, **75**, 1011 (1953).

[4] "Handbuch der Präparativen Anorganischen Chemie," F. Enke, Stuttgart, 1953, Vol. II, p. 901.